

ISSN: 1991-8941

## **A new approach to the prediction of the hybridization of a p-block central atom and the final geometrical structure of a molecule or an ion**

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**Abstract.** This paper describes simple rules that can minimize the uncertainties in explaining the process of finding the hybridization of a p-block central atom and the geometrical structure in a covalent molecule or an ion. The current rules to predict the hybridization and geometrical structure are based on Lewis's structure, Pauli's principle, covalent bond theories and the VSEPR model. This is a practical and easy way used by teachers and students.

**Keywords:** Covalent bond, Hybridization, Lewis structure, Main-Group Elements, VSEPR.

### **Introduction**

Molecular geometry and hybridization are still interesting themes for chemists [1,2]. They play an important role in the teaching of students to improve a reasonable imagination concerning the shape of molecules and ions through the understanding of the covalent bond theories[3]. However, all bonding theories indicate that the hybridization of orbitals is just a model and should not be taken as a real phenomenon [4].

Our present work describe a simple reasonable method that helps students and teachers to figure out the hybridization for a p-block central atom in a molecule or ion, meanwhile some inorganic and general chemistry textbooks missed such practical method, showing a short clarification concerning our present aspect of inorganic chemistry[5,6]. In respect with this subject, many students and lecturers encounter difficulties in predicting hybridization toward a reasonable geometrical structures. Furthermore, countered difficulties are also experienced in getting a clear picture by using the above theories and models of the covalent bond.

Indeed, teaching books are focusing on some known structural determination of simple molecules like H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub> and CO<sub>2</sub>, etc., by applying different propositions. Some teaching books are using the concept of hybridization on the bases of Molecular Orbital Theory (MOT) as a unique method to explain the molecular

structures[7]. This method offers a satisfactory explanation for simple molecules (of two atoms) and also the spectroscopic and magnetic properties of transition metals complexes. For comparison purposes, it has been reported that the MOT calculations has more complicated determinations than the Valence Bond Theory (VBT), especially in compounds or ions that consist of more than two atoms.

This paper deals only with the elements of the main group (p-block) and introduces a simple method for prediction of the hybridization and the geometrical structures of molecules and ions.

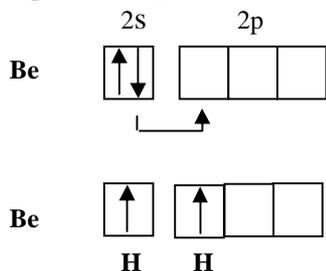
A correct hybridization and structural prediction can be obtained through the combination of Lewis definition of covalent bond[8], the VBT of Pauling and the VSEPR model of Giellspie [9].

### **Prediction procedure**

#### **Rule 1**

The central atom must initially be determined. Such atom is a provider of enough unpaired electrons to share and saturate the valence shell of the joined peripheral atoms. The valence orbitals of these peripheral atoms will be saturated, so as to possess the same electronic configuration (outer shell) of that of the nearest "noble gases" atom, as shown in example 1.

**Example 1. BeH<sub>2</sub>**

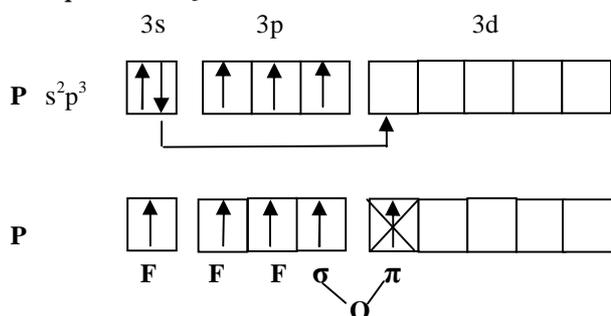


The Beryllium atom has sp hybridization and the final shape of the BeH<sub>2</sub> molecule is linear. Similarly, it is easy to predict the molecular shapes of the compounds (BF<sub>3</sub>, CH<sub>4</sub>, PF<sub>5</sub> and SF<sub>6</sub>) as mentioned in most inorganic chemistry books.

**Rule 2**

Any π-bond in a molecule or ion is ignored and not considered in the hybridization of the central atom. However, it must be shown in the final shape of the structure. The π-bond will be better oriented in the last shared orbitals of the central atom and neglected in order to justify the correct hybridization.

**Example 2. POF<sub>3</sub>**

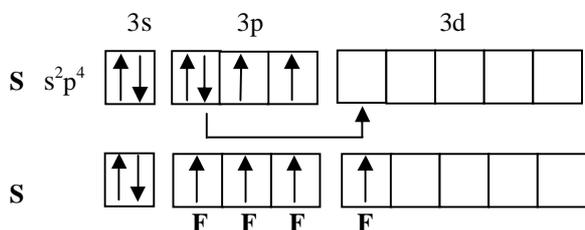


The hybridization of the phosphor atom is sp<sup>3</sup> and not sp<sup>3</sup>d as it appears. The resulting shape of POF<sub>3</sub> is tetrahedral.

**Rule 3**

The non-bonding of electrons (lone pair(s)) on a central atom is to be counted with the bonding pairs for the purpose of predicting its hybridization pattern.

**Example 3. SF<sub>4</sub>**

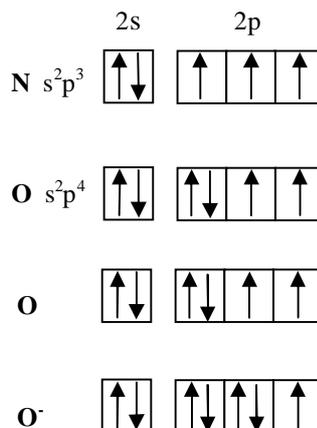


The hybridization of the sulphur atom is sp<sup>3</sup>d and the molecular shape of SF<sub>4</sub> is distorted tetrahedral (Disphenoid).  
Rule 4

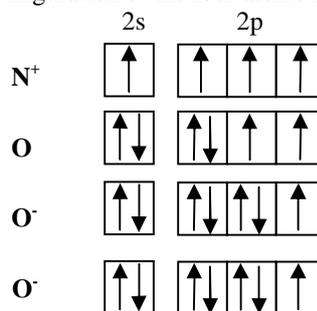
In a molecule or an ion with a central atom belonging to the second period in the periodic table, the promotion of

electrons from the s- and p-orbitals to a d-orbital is forbidden due to the absence of the 2d-orbitals.

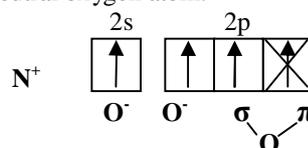
**Example 4. NO<sub>3</sub><sup>-</sup>**



By losing an electron from p-orbital and promoting one from s-orbital, the nitrogen atom will have four unpaired electrons. At the same time, the lost electron will be gained by one of the two neutral oxygen atoms. The electronic configuration of the four atoms may occur as the following:



The nitrogen atom links with the two negative oxygen atoms by two σ- bonds and the σ- and π- bonds with the third neutral oxygen atom.



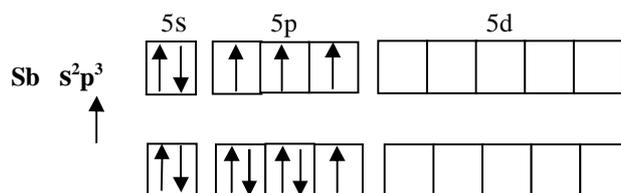
By neglecting the π-bond according to rule 2 the hybridization of the central atom is sp<sup>2</sup> and the geometrical structure of the nitrate ion is trigonal planar.

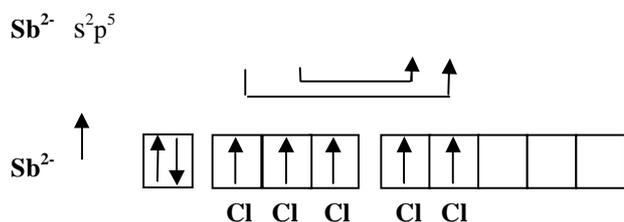
**Rule 5**

a- In case of ions (negative or positive), electrons are gained or lost by the central atom and the charge will appear on this atom.

i- Negative ions

**Example 5. SbCl<sub>5</sub><sup>2-</sup>**

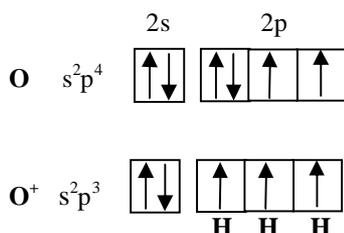




The hybridization of the central atom is  $sp^3 d^2$  and the shape of  $SbCl_5^{2-}$  is square pyramid.

ii- Positive ions

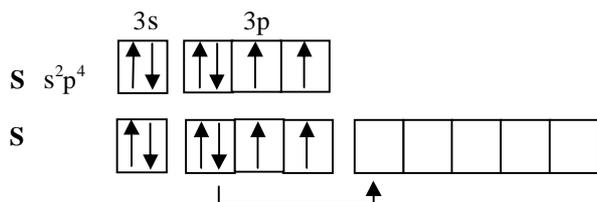
Example 6.  $H_3O^+$



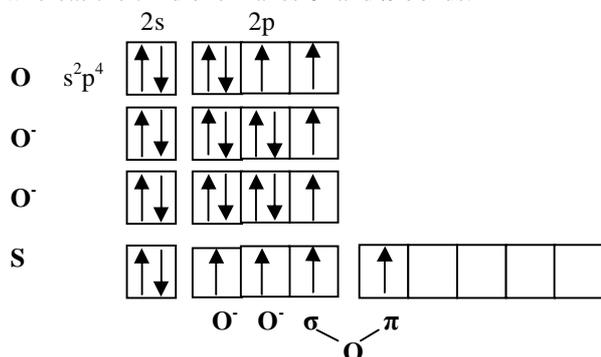
The hybridization of the oxygen atom is  $sp^3$  and the structure of  $H_3O^+$  is trigonal pyramid.

b- In case of a negative ion with two or more peripheral atoms (O, S, etc.) having resonating electrons with the central atom as in  $SO_3^{2-}$ ,  $S_2O_3^{2-}$  and  $PS_2Cl_2^-$  [10], the negative charges must appear on the peripheral atoms. The  $\pi$ -bonds and hence the negative charges will be delocalized between the peripheral atoms and the central atom.

Example 7.  $SO_3^{2-}$



Out of the three oxygen atoms, two of them will gain a negative charge each forming  $\sigma$ -bond with the sulphur atom, whereas the third one makes  $\sigma$ - and  $\pi$ -bonds.



The hybridization of the central atom is  $sp^3$  and the final structure of  $SO_3^{2-}$  is trigonal pyramid.

Discussion

Despite the fact that the hybridization of the central p-block atoms in molecules and ions has thoroughly been investigated, controversial and inaccurate final structures have often been debated by students and teachers. In this work there is a large accuracy to predict the hybridization and the geometrical structure based on the previous rules.

According to Rule 1, the principal factor that determines the number of unpaired electrons, provided by the central atom, are the peripheral atoms. This enables them to get the "noble gases" configuration. An example of the above sentence, are the molecules  $SF_2$ ,  $SF_4$  and  $SF_6$ . The unpaired electrons which are provided by the central atom (sulphur) are 2,4 and 6 respectively.

As in Rule 2, an easier interpretation of the hybridization of the central atom by following the proposition of ignoring the  $\pi$ -bond [11] in comparison to the Gillespie's Model which consider both  $\sigma$ - and  $\pi$ -bonds as a single bond, combined with the idea of bent bond and electron-pair domain model [12]. However, both arguments are considered as proposition and not a real occurrence.

The Rule 2 is also valid for structures containing more than one  $\pi$ -bond.

The electron pairs in Rule 3 must oriented according to VSEPR model [9] to get the correct shape.

The prime reason for a central atom to create a specific number of unpaired electrons (example of positive nitrogen atom in Rule 4), via promotion or loss of electrons, is determined by the extent of electronic requirements of the peripheral atoms "outer shells" by filling their valence shell orbitals as depicted in the previous examples. Evidently, the pentacoordinated central atom in  $NH_5$  or  $NH_4X$  compounds (where  $X = Br, Cl, OH$ ) dose not exist [13].

According to the Rule 5, the prediction of the geometrical shapes of ions with more than one oxygen atom and having one or more  $\pi$ -bonds, such as  $ClO_2^-$ ,  $NO_2^-$ ,  $CO_3^{2-}$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $ClO_3^-$ ,  $ClO_4^-$  ...etc., will be much easier to explain with greater accuracy.

In  $ClO_2^-$  as example, the bond length of Cl-O was found experimentally to be 1.56 Å [14,15], indicating a bond order of 1.5 as a result of the formation of a  $\sigma$ - and  $\pi$ -bonds. This finding coincides with the proposition of Rule 5-b, that the negative charges must appear on the peripheral atoms rather than the central atoms. Therefore, the delocalization of the negative charge tend to favor the peripheral atom to the central one, whereby the bond order would have been 2, which is not in consideration.

However, the resulting hybridization of the central atom in both cases is always  $sp^3$  and the shape is V-shape. The final structures of molecules or ions that are predicted by considering the above rules, must show all the relevant details; charge(s),  $\sigma$ - and  $\pi$ -bond (s) and the lone pair (s) of electrons as in the previous examples.

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### طريقة عملية جديدة لاستنتاج التهجين لذرة مركزية تعود لعناصر p-block مع استنتاج التركيب الهندسي النهائي للجزيئة او الايون

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#### الخلاصة

يصف هذا البحث قواعد بسيطة والتي عند تطبيقها يمكن تضيق هامش الخطأ إلى أقصى حد عند تحديد التهجين لذرة مركزية تعود إلى عناصر الزمر الرئيسية (p-block) في أيون أو مركب تساهمي بالإضافة إلى الشكل الهندسي النهائي. أن هذه القواعد تعتمد أساساً على تركيب لويس ومبدأ باولي وكذلك نظرية الاصرة التساهمية بالإعتماد على فكرة تناظر المزدوجات الالكترونية في الاغلفة التساهمية (VSEPR) لغرض إيجاد تهجين الذرة المركزية في أيون أو مركب وكذلك التركيب الهندسي. أن الطريقة المذكورة هي طريقة عملية وبسيطة ويمكن استخدامها من قبل الطلبة والأساتذة.